

FIGURE 1. Formation of chlorinated (a), bromochloro (b), and brominated (c) HAAs as a function of bromide ion concentration in chlorinated Myrtle Beach extract, pH 8.

concentrations. MCAA and MBAA, which are not included in these diagrams, individually constituted less than 5% of the total molar concentration of HAAs in all cases. At low bromide concentrations ( $<3 \mu\text{M}$ ), speciation is generally in the order:  $\text{TCAA} > \text{DCAA} > \text{BrCl}_2\text{AA} > \text{BrClAA} > \text{Br}_2\text{ClAA} > \text{DBAA} > \text{TBAA}$ . At the high end of the bromide range studied ( $>20 \mu\text{M}$ ), speciation is in a nearly opposite order:  $\text{TBAA} > \text{DBAA} > \text{Br}_2\text{ClAA} > \text{BrCl}_2\text{AA} > \text{BrClAA} >$

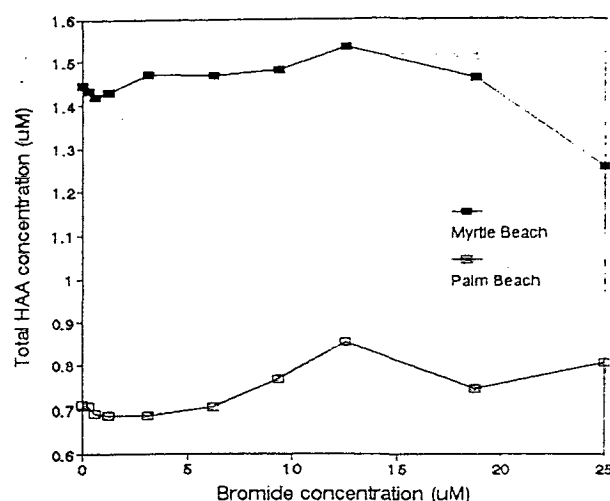


FIGURE 2. Total HAA formation as a function of bromide ion concentration in chlorinated extracts, pH 8.

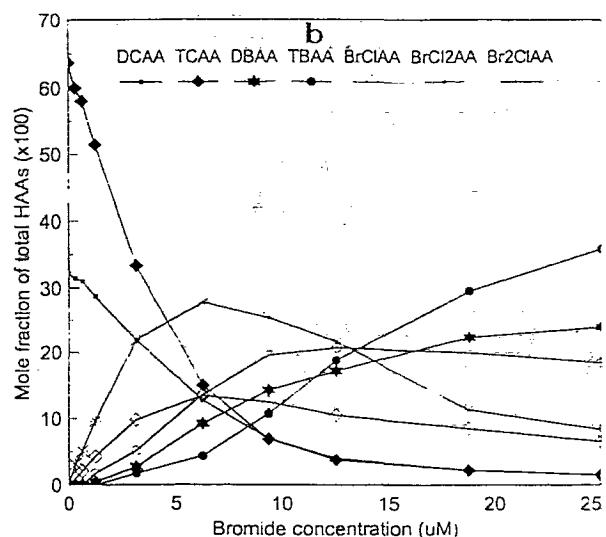
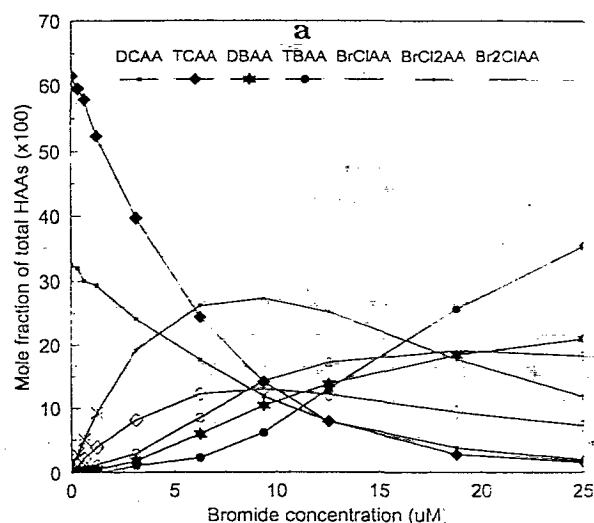


FIGURE 3. Distribution of individual HAA species in chlorinated Myrtle Beach (a) and Palm Beach (b) extracts, pH 8.

DCAA, TCAA. These observed patterns of HAA speciation are qualitatively similar to the results reported previously by Pourmoghaddas et al. (8) for the chlorination of commercial humic acid in the presence of bromide ion.

5MM=  
400 μg/L  
Br<sup>-</sup>

TABLE 1

## Haloacetic Acids in Finished Drinking Waters

HAA	PSWC TOC = 2.6 mg/L Br <sup>-</sup> = 50.6 µg/L (0.63 µM)		Houston <sup>a</sup> TOC = 4.9–8.8 mg/L Br <sup>-</sup> = 72–134 µg/L (0.90–1.68 µM)		MWD TOC = 3.3 mg/L Br <sup>-</sup> = 220 µg/L (2.75 µM)		Corpus Christi TOC = 4.7 mg/L Br <sup>-</sup> = 412 µg/L (5.16 µM)	
	µg/L	mole fraction	µg/L	mole fraction	µg/L	mole fraction	µg/L	mole fraction
MCAA	BDL <sup>b</sup>	0.00	1.29	0.06	1.17	0.04	BDL	0.00
DCAA	2.15	0.10	12.7	0.45	7.02	0.19	5.45	0.23
TCAA	18.4	0.70	6.89	0.19	5.07	0.11	1.41	0.05
MBAA	BDL	0.00	BDL	0.00	1.78	0.04	BDL	0.00
DBAA	BDL	0.00	BDL	0.00	9.18	0.14	8.39	0.21
TBAA	BDL	0.00	BDL	0.00	BDL	0.00	BDL	0.00
BrCIAA	BDL	0.00	4.62	0.12	10.8	0.21	6.73	0.21
BrCl <sub>2</sub> AA	6.55	0.20	5.28	0.12	12.2	0.20	8.75	0.23
Br <sub>3</sub> CIAA	BDL	0.00	2.60	0.05	5.37	0.07	3.52	0.08
ΣHAA5	20.6		20.9		24.2		15.3	
ΣHAA9	27.1		33.4		52.6		34.3	

<sup>a</sup> Houston, TX, finished drinking water was produced from a blend of two source waters. <sup>b</sup> BDL, below detection limits.

of the total HAAs on a mole fractional basis in the finished water from PWSC, which contained only 50.6 µg/L (0.63 µM) Br<sup>-</sup> in the source water. These results confirm the laboratory findings that the three bromochloro species are significant species formed during the chlorination of bromide-containing waters. It should be noted, however, that the stability of the more highly brominated HAA species has been questioned (23). Additional research is needed to determine the degree to which these species persist in water distribution systems.

## Discussion and Conclusions

**HAA Formation and Speciation in Chlorinated Extracts.** The results of the chlorination studies suggest that bromochloro HAA species are readily formed from the chlorination of humic substances in the presence of bromide ion. In the present study, these species constituted at least 10% of the total HAAs in waters containing as little as 1.2 µM Br<sup>-</sup> (0.1 mg/L). In this region of fairly low bromide concentration, the principal species observed, in order of significance based on quantitative formation, were TCAA, DCAA, BrCl<sub>2</sub>AA, and BrCIAA. At higher bromide concentrations, in the range of 6–15 µM Br<sup>-</sup>, BrCl<sub>2</sub>AA was the principal species formed. The presence of the bromochloro species at significant levels relative to other HAA species was confirmed in finished drinking waters. These species are not currently regulated in drinking water, and their health effects and occurrence are not known. The results of this study suggest that these compounds are likely to be present in typical chlorinated drinking waters at significant concentrations. It is likely that characterization of the total HAA concentration by measurement of only MCAA, DCAA, TCAA, MBAA, and DBAA concentrations, as specified in the proposed Disinfectants/Disinfection Byproducts Rule, is an incomplete description of and may appreciably underestimate the overall presence of HAAs in finished drinking waters. This issue may be of particular concern to utilities treating waters with relatively high bromide concentrations (>0.2 mg/L), where the bromochloro species may well constitute more than 50% of the total HAA concentration.

HAA speciation is dependent on the ratio of bromide ion to chlorine. Speciation was similar for the two aquatic

extracts studied, and this suggests that the effect of bromide ion on HAA speciation may be independent of the source of natural organic material. The two extracts showed similar speciation patterns despite the fact that Myrtle Beach extract appeared to be approximately two times as reactive as Palm Beach extract in terms of quantitative HAA formation from chlorination. Smooth curves were observed for the patterns of HAA formation as a function of bromide ion concentration. There are several other factors that were held constant in this study that may also influence HAA speciation. These factors include chlorine dose, reaction time, TOC concentration, and reaction temperature.

Decreasing the pH of chlorination appeared to have a greater impact on increasing the formation of di- and trihalogenated species containing bromine as compared to species containing only chlorine. This may reflect lesser stability of the species containing bromine in environments of elevated pH or greater substitution reactivity of HOBr relative to HOCl at lower pH.

In chlorinated waters, the two extracts showed nearly identical HAA speciation into mono-, di-, and trihalogenated species, both at pH 8 and pH 6. In the absence of bromide, relative formation of TCAA compared to DCAA on a weight basis was approximately 2.4:1. This was under chlorination conditions of 2 mg of chlorine as Cl<sub>2</sub>:1 mg of TOC. These results are similar to those reported previously by Miller and Uden (26) of a weight ratio of TCAA/DCAA ≈ 2.25 at a chlorine to carbon weight ratio of 2. One might expect a different distribution at a different chlorine to carbon ratio. Miller and Uden (26) showed that relative formation of TCAA and DCAA is dependent on chlorine dose, with the more highly chlorinated species being favored by high chlorine dose. These observations suggest that the formation of di- and trihalogenated HAA species may proceed through common dihalogenated intermediates that can either be oxidized or hydrolyzed to the dihalogenated HAA species or further halogenated to form the trihalogenated HAA species. This idea is similar to the mechanisms of HAA formation that have been proposed by Reckhow and Singer (27). The present study suggests that different sources of natural organic material may behave similarly in this respect, and the finding that the distribution of mono-, di-, and trihalogenated species is independent of Br<sup>-</sup> concentration suggests that the HAA species containing